

Micro-characterization of KDP Etch Pits

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INTRODUCTION

Potassium Dihydrogen Phosphate (KDP) is a non-linear optical material used for laser frequency conversion. KDP is typically diamond machined, annealed and then coated with a silica sol-gel. Previous investigations show that because the porous sol-gel coating absorbs water from the air, dissolution pits form when the KDP crystals are exposed to ambient humidity. The porous sol-gel coating provides a reservoir of water and wicks up the dissolved KDP. Previous results have also shown that the morphology of the surface defects is determined by the cut of the crystal and the crystallographic axes. Controlling the density and size of these defects is paramount to producing reliable optics that are not susceptible to laser light damage.

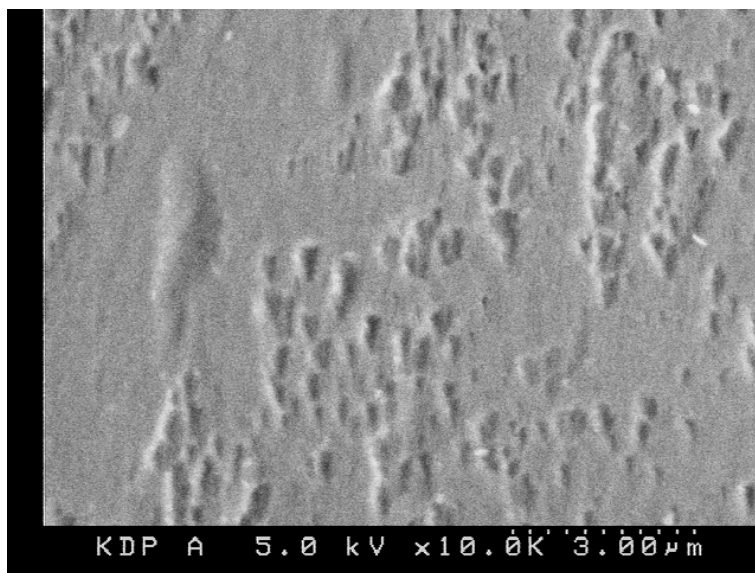


Figure 1. Annealed diamond turned KDP surface with triangle shaped etch pits created in a 1kV sputter etched area by 10 min. ultrasonic treatment in reagent grade ethanol.

EXPERIMENTAL

The spatially resolved x-ray photoemission/absorption station (μ XPS and μ XANES) on branch line 7.3.1.2 was used to examine the chemistry inside an etch pit and compare it to the nominal surface chemistry. Photoemitted electrons were analyzed using a hemispherical energy analyzer. Photoemission spectra were collected with $h\nu=550$ and 790 eV. The combined energy resolution of the monochromator and the analyzer was $\Delta E \approx 0.5$ eV. Binding energies were referenced to the

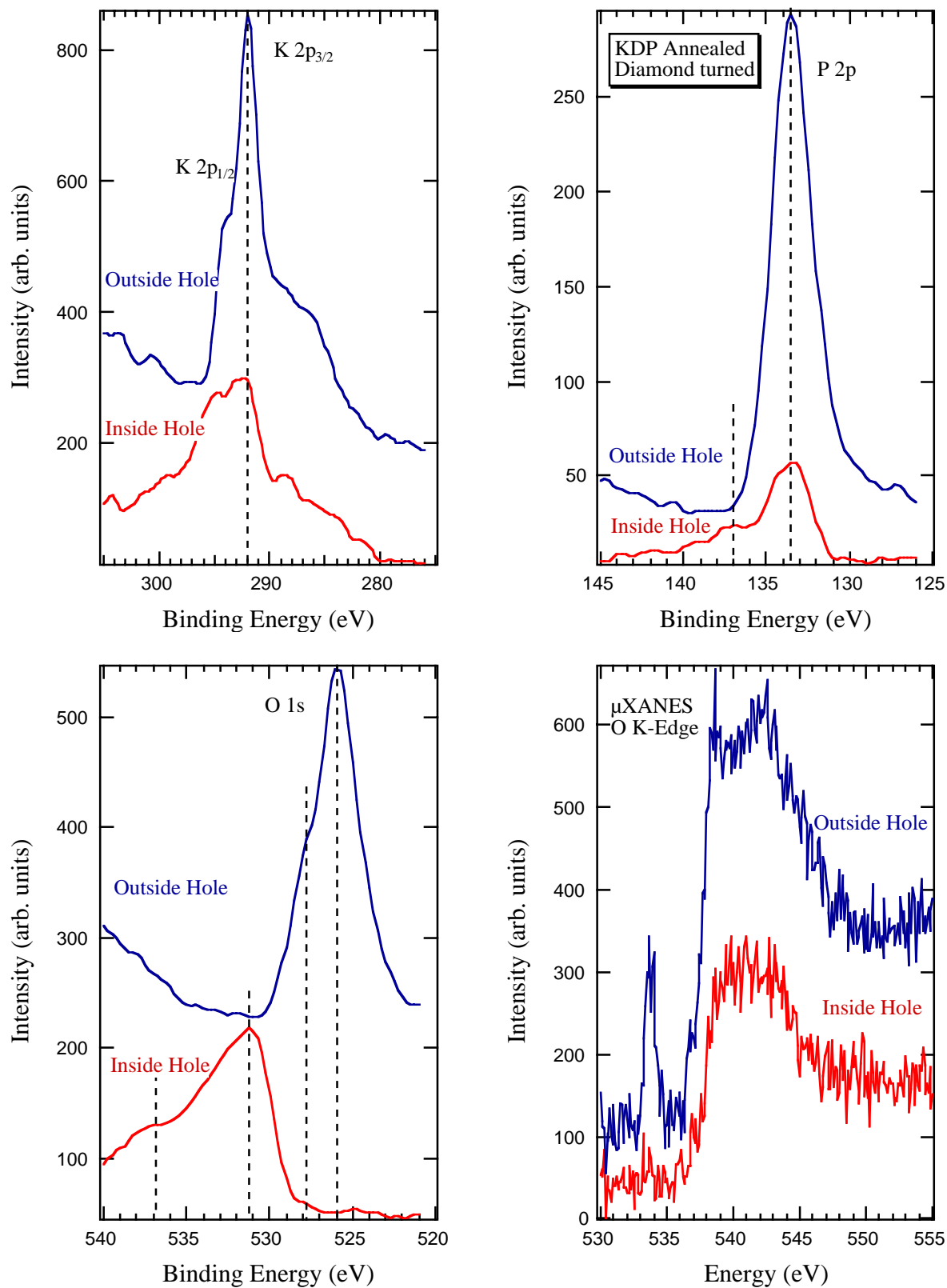


Figure 2. K 2p, P 2p and O 1s μ XPS core-level spectra, and O K-edge μ NEXAFS spectrum of diamond turned and annealed KDP, inside and outside of an etch pit.

C 1s photoelectron line arising from adventitious carbon to account for charging effects. The O K-edge XANES were acquired by monitoring the total electron yield (TEY). Prior to analysis, residual surface contamination was removed by *in-situ* sputtering with 500 eV Ar⁺ ions rastered over a 0.5 x 0.5 mm area.

RESULTS

The K 2p, P 2p and O 1s μ XPS core-level spectra, and O K-edge μ XANES spectrum of diamond turned and annealed KDP, inside and outside of an etch pit, are presented in Figure 2. The binding energies of the K 2p_{3/2,1/2}, P 2p_{3/2,1/2} and O 1s core-levels measured outside the hole are in agreement with our laboratory XPS measurements for bulk KDP. However, the μ XPS measurements inside the hole indicate distinct chemical variations. Specifically, the P 2p_{3/2,1/2} spectrum measured inside the hole has a second component shifted 3.5 eV to higher binding energy. This chemical shift is indicative of P₂O₅. [1,2] In addition, the O 1s core-level measured inside the hole is shifted \approx 5 eV to higher binding energy supporting the presence of P₂O₅ inside the hole. [2]

The O K-edge μ XANES also reveal distinct chemical differences in and out of the hole. Specifically, the excitonic peak at 533.7 eV usually attributed to double bonded oxygen, is much larger outside the hole and may be indicative of an ortho- or pyro-phosphate phase. [3,4] In addition, the spectral differences observed indicate that the O atom is coordinated by a different number and type of ligand between the two locations.

KDP is a stable phase in the K₂O–P₂O₅–(H,D)₂O ternary phase diagram and is grown from solution. If there was residual P₂O₅ on the surface following growth and, knowing that P₂O₅ is very hygroscopic readily forming phosphoric acid (H₃PO₄), one could begin to surmise that the holes or ‘etch pits’ are due to chemical etching. Our results support this preliminary hypothesis.

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